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Abstract

RADIATION CHEMISTRY IN ALKALINE SOLUTIONS

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The oxyanions of manganese proved to be a particularly convenient object of investigations of the radiolysis of the alkaline solutions, because the hydrolyses complicating the reaction do not occure here. The reduction of permanganate under gamma irradiation /^{60}Co about 200 c activity/ proceeds successively: $MnO_4^- \longrightarrow MnO_4^{2-} \longrightarrow MnO_4^{3-} \longrightarrow MnO_2$. Each subsequent stage occurs after the preceding one has been finally accomplished. Thus it was possible to investigate seperately each of these stages by selecting the suitable concentration of OH^- ions. The radiation yield of each particular stage in alkaline solutions may be expressed as below: $G(-MnO_4^{n-}) = G_H + 2G_{H_2O_2} - G_{OH} = 1.9$ equivalents per 100 eV. This yield is much lower than in neutral solutions, which is due to the fact that OH radicals occur here in their proper role of oxidizing agents. They oxidize all manganese oxyanions in which manganese is on a lower than +7 oxidation state. In neutral solutions OH radicals participate directly in the reduction of permanganate, thus causing the yield increase in comparison with alkaline solutions. They cause also the yield dependence on the initial concentration of permanganate. This yield is expressed by an empirical expression: $G(-MnO_4^-) = 1.7 + 1.62 \cdot 10^2 MnO_4^{-\,1/2}$, which has been also theoretically derived.

This twofold role of OH radicals e.g. as oxidizing and reducing agents, has been confirmed also in the radiolysis of potassium iodide solution. OH radicals oxidize I^- to I_2 and reduce the hypoiodite formed in neutral or alkaline solutions with I_2. Thus, OH radicals induce the considerable increase of the radiation yield with the increase of the initial I^- concentration, while causing its decrease with the increase of pH.

In alkaline solutions the radiation yield of the reduction of manganese oxyanions does not depend on the initial concentration of oxyanions nor on the concentration and type of hydroxide. Hence the general conclusions have been drawn concerning the model of radiolysis of the alkaline solutions in which the radicals are formed directly from OH^- and Me^+ ions. This model has been confirmed also in the radiolysis of the chromate and chromite solutions. In these solutions the chromites are oxidized to chromates by gamma rays. Chromates however, are reduced to chromites only in solutions saturated by hydrogen with a yield which depends on the concentration ratio CrO_2^- to H_2.

On the basis of the proposed mechanism of the radiative reduction of manganate in concentrated alkaline solutions the following molecular yields in these conditions have been calculated: $G_{H_2} = 0.12$; $G_{H_2O_2} = 0.51$